



Diffusion of Atoms in Semiconductors Elucidated

Large Disparity Between Ga and Sb Self-Diffusion in GaSb Seen

A research team led by Eugene Haller has provided important new insights into self-diffusion in solids. In a paper published in *Nature*, they reported their discovery that in the semiconductor gallium antimonide (GaSb) the diffusion coefficient of antimony is at least 1000 times smaller than that of gallium. A completely new diffusion mechanism may be responsible for this unexpected phenomenon.

The most fundamental mass transport process in solids is self-diffusion, the natural movement of individual atoms within the material. It was first suggested in the 1920's that this process does not occur through the simple exchange of positions of two neighboring atoms, but rather, must be mediated by defects. In metals and in some semiconductors, it has been shown that vacancies (missing atoms) are the most important such defect. In this so-called "vacancy mediated diffusion," an atom diffuses by moving into a neighboring vacancy, leaving behind a vacancy in its former position. [Another important diffusion mechanism in semiconductors involves motion of atoms located between lattice sites (self-interstitials).]

Historically, it has been difficult to measure self-diffusion rates accurately in solids, in part because of the need to label some but not all of the atoms in a pure material. Radioactive isotopes are often used for this purpose but are limited by their short half lives. Another difficulty is that diffusion rates are highly sensitive to the quality of the crystal under study; for accurate measurements material of high crystalline quality is required. For these reasons, even for silicon, accurate measurements have been available only in the last 10 years. Self-diffusion in compound semiconductors has an additional level of complexity; the two elements might have different diffusion coefficients.

The Haller group performed these self-diffusion measurements using highly enriched stable isotopes as labels. Compared to the radioactive probe approach, diffusion studies with stable isotopes are neither limited by the half-life of the isotope nor affected by the degradation associated with the implantation or deposition of the isotopes. Thus, experiments can be extended to much longer times and conducted over a wider temperature range.

GaSb offers a unique opportunity for this type of experiment. Two stable isotopes exist for both Ga (^{69}Ga and ^{71}Ga) and Sb (^{121}Sb and ^{123}Sb), allowing the simultaneous study of diffusion of Ga and Sb on their respective sublattices. A collaborating team from Spain grew a special test structure of high crystalline quality: a natural GaSb substrate under a 100 nm layer of $^{71}\text{Ga}^{123}\text{Sb}$ under a 100-layer of nm $^{69}\text{Ga}^{121}\text{Sb}$ under a 200-nm natural GaSb cap (see figure). To measure the self-diffusion, the team annealed the structure at various temperatures and measured the movement of the isotopically labeled atoms into the neighboring layers via ex-situ secondary ion mass spectrometry (see figure). The results were surprising: Ga atoms diffused much faster than Sb atoms: Ga diffusion could be measured at temperatures as low as 575 °C while little Sb diffusion was observed even after 18 days at 700 °C only 12 °C below the melting point. The observed thousandfold asymmetry of the self-diffusion on the two sublattices is extraordinary.

This discovery is unprecedented in the field. Similar disparities in self-diffusion rates of compounds have been seen in some transition metal silicides, but in these systems the diffusion coefficients of the two elements approach each other near the melting point. The team has hypothesized that the Ga and Sb atoms diffuse independently, each on its own sublattice. The temperature dependence of the Ga self-diffusion coefficient is consistent with that predicted for Ga-vacancy-mediated diffusion. The situation with Sb is different, however. If an Sb vacancy tries to form, the electronic properties of GaSb make it favorable for a neighboring Ga to fill it by forming a so-called Ga "antisite" defect. Surrounded by its 4 Ga neighbors, the Sb vacancy is therefore unstable and cannot mediate Sb diffusion. Other diffusion pathways apparently are also slow.

The results may be applicable to other III-V and II-VI compound semiconductors, and are expected to inspire new thinking into the self-diffusion mechanisms in these materials. The discovery may have important ramifications in that the manufacturing and operation of all semiconductor-based microelectronic devices, including microprocessors and optoelectronic devices, relies critically on the control of diffusion processes. For example, controlled diffusion is required for the introduction of impurity atoms to certain areas of semiconductors to create the three-dimensional structures required to enable electronic function. On the other hand, diffusion processes must be understood and controlled such that these 3-D structures are maintained during thermal processing and device operation.

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H. Bracht, S. P. Nicols, W. Walukiewicz, J. P. Silvera, F. Briones, and E. E. Haller, "Large disparity between gallium and antimony self-diffusion in gallium antimonide," *Nature* 408, 69-72 (2000).